

UC BERKELEY COLLEGE OF CHEMISTRY

CHEMISTRY 4BL

GENERAL CHEMISTRY AND QUANTITATIVE ANALYSIS

Quantitative Analysis of a Co/Cu Solution

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1 Abstract

In this lab, we used several analysis techniques to separate and find the quantities of cobalt and copper in an unknown solution. In the first week, we used chromatography with an anion-exchange resin to separate the copper and the cobalt from the rest of the solution. In the next week, we used backtitration with EDTA as a chelating agent to find the concentration of cobalt in our sample. In the final week of our lab, we used atomic emission spectroscopy to analyze the absorbance of our copper sample to calculate the concentration. We calculated the concentration of cobalt in our sample to be $87.6\text{mM} \pm 14.7\%$, and the concentration of copper in our sample to be $192.3272\text{mM} \pm 2.47887\%$.

2 Introduction

Analytical Chemistry can be said, in general, to be an answer to the dual questions “What is it?” and “How much is there?”. In this lab, we aimed to answer the former question by separating our unknown solution into fractions using a technique called Anion-Exchange Chromatography (Figure 1), and the latter question through the use of Complexometric Back-titration (Figure 2) and Atomic Emission Spectroscopy (Figure 3). We believed that our results could be tabulated far more precisely using the (automated and fine-tuned) Atomic Emission Spectrometer than compared to the Complexometric Titration, which relies on human operation and interpretation of an indicator.

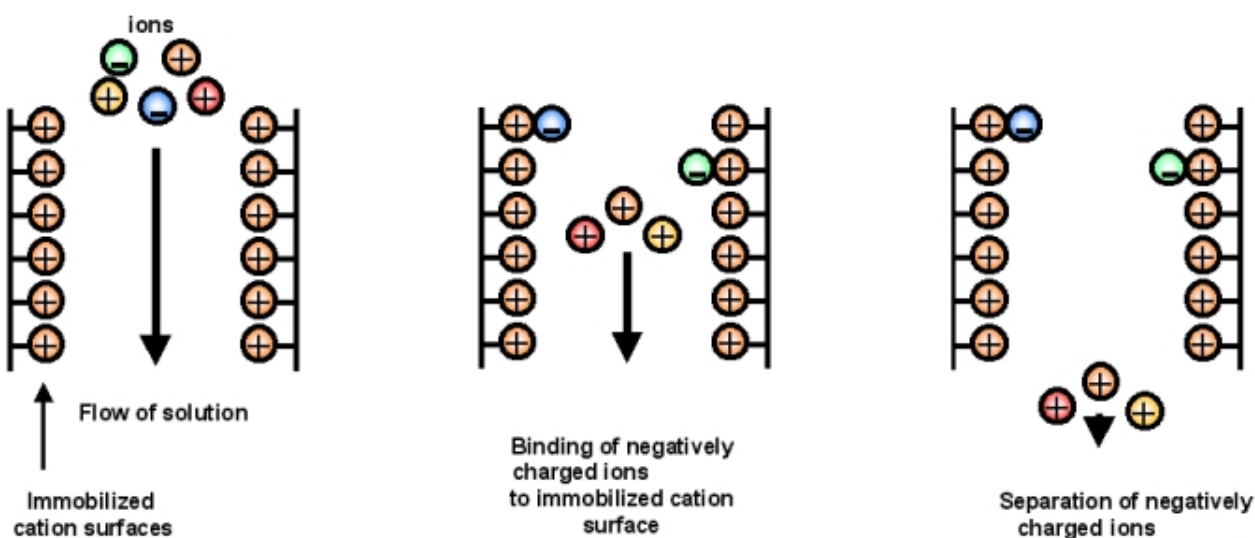


Figure 1: Anion-Exchange Chromatography. Two ions enter, one ion leaves.^[4]

2.1 Anion-Exchange Chromatography

In *Anion-Exchange Chromatography* (Figure 1), a cationic resin is used as the stationary phase to separate the eluent. As the eluent enters the column, any anions in solution are more tightly bound by the positive resin, and as such are functionally “stuck” to the resin far longer than their cationic or neutral counterparts. As a result, negative ions take much longer to elute, and are functionally separated from neutral compounds or positive ions.

However, there is a fundamental flaw in the application of this process to the separation of copper and cobalt ions—both are naturally found in the +2 oxidation state, and as such cannot be separated by this method! We can get around this restriction by using chloride ligands to change the prevalent

forms of the metal ions. As it turns out, at the right concentration of Cl^- ions (3.0 M to be precise), almost all of the copper will exist in (anionic) CuCl_3^- or CuCl_4^{2-} forms, while nearly all of the cobalt will remain as positively charged Co^{2+} or CoCl^+ . This means that the anion-exchange resin was completely capable of retaining Cu in the stationary phase long enough for it to visibly separate from the Co.

2.2 Complexometric Back-titration

Once we had separated the ions, the next step was to calculate the concentrations of the ions we had eluted (you might say it was time to put the “quantitative” in “quantitative analysis”). We worked on finding the amount of cobalt first. There are many possible ways to analyze different samples (for example, we could have precipitated the cobalt directly using oxalic acid to form CoC_2O_4), but in this case, we elected to utilize a *complexometric titration*. This is a specific type of titration where the titrant used is a *chelating agent*, which forms multiple bonds to and thereby isolates the titrate (which is usually a metal ion). In most complexometric titrations, the titrant is EDTA (a humane abbreviation for **E**thylenedi**a**minet**e**tetra**a**ctic **A**cid) (Figure 2), a molecule that can bind with a donor atom up to 6 times, and is an especially effective agent for sequestering metals.

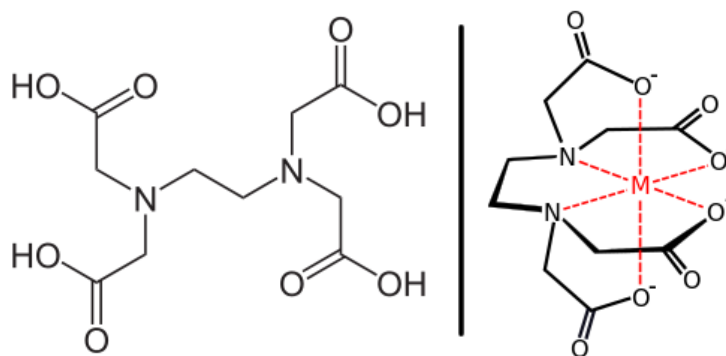


Figure 2: EDTA, both free (left) and in a metal complex (right)^[5]

To determine the endpoint of a titration, an indicator is necessary; however, a standard titration of EDTA and Co^{2+} does not have a very distinct endpoint via the indicators we have on hand. We can skirt this issue by using a titration technique known as *back titration*, in which we add excess EDTA to our Co^{2+} unknown, then perform a titration with a Co^{2+} standard. Note that we are functionally titrating our chelating agent with a standardized concentration of our unknown, instead of the other way round. The reverse reaction here has an endpoint that we can identify far more easily, using the thiocyanate ion (KSCN^-) as an indicator. Once we have found the equivalence point, the moles of Co^{2+} standard we used are equal to the *excess* amount of EDTA added to the unknown; the actual amount of EDTA added minus the excess gives the original amount of Co^{2+} ion neutralized by the EDTA.

2.3 Atomic Emission Spectroscopy

Finally, we began work on calculating the concentration of Cu^{2+} in the solution. To this end, we utilized an instrument known as an *Atomic Emission Spectrometer* and a set of Cu^{2+} standards of known concentration. In Atomic Emission Spectroscopy (AES), a (very dilute) solution of sample is sprayed into a mist, which is mixed with acetylene and air to produce a very flammable gas mixture. This mixture is combusted, and the spectra of the resulting flame is analyzed; because AES is mostly

automated nowadays, spectrometers are often set to screen for specific wavelengths of light that correspond to the specific elements being looked for. By comparing the emission strengths at these certain wavelengths, a set of known standards can be used to create a calibration curve, which makes finding the concentration of an unknown solution trivial given its absorbance at a specific wavelength.

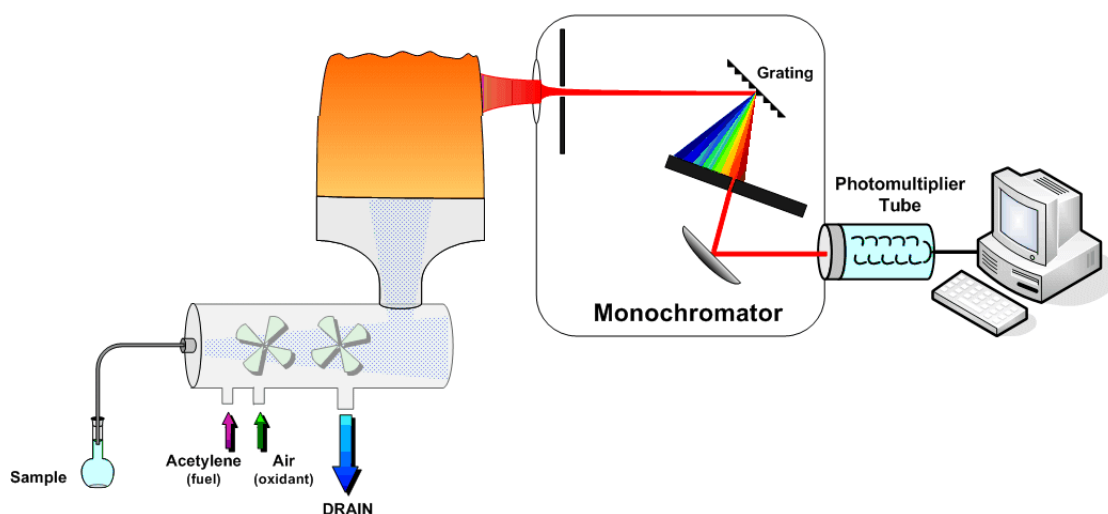


Figure 3: Diagram of an Atomic Emission Spectrometer^[6]

3 Methods

3.1 Anion-Exchange Chromatography^[1]

We began our chromatography by setting up our elution column. We obtained an ion-exchange column and acid-washed it, along with all of our other glassware. We then filled it with AG 1-X8 resin by adding an acid slurry of resin, waiting for it to settle, then vacuuming up the excess acid and adding more slurry. We repeated this until our column was filled until approximately the 18 mL mark. Using a funnel to avoid disturbing the resin surface, we carefully pipetted 1 mL of our unknown solution into the column and opened the column. We kept the column well-stocked with excess 3M HCl above the resin line such as to keep the Cl^- concentration high and the Cu^{2+} in the stationary phase. When the bluish-green Co^{2+} band approached the bottom of the column, we began collecting the eluent. Once the slower yellow Cu^{2+} band approached the base of the column, we stopped collecting eluent and added 2 mL of deionized water in order to decrease the Cl^- concentration and speed the elution of Cu^{2+} , then began collecting the eluent in a new container. Approximately 2 minutes after the Cu^{2+} band disappeared from the column, we added a new sample of unknown and began the process over again. In total, we collected 3 different samples each of Co^{2+} and Cu^{2+} . Finally, we diluted the Cu^{2+} solutions by a factor of 100 in a volumetric flask, and stored them away for part 3 of our experiment.

3.2 Complexometric Back-titration of Co^{2+} ^[2]

We began our titration by preparing our Co^{2+} and EDTA standard solutions. We took our stock solution of Co^{2+} , which contained $9.26163 \frac{\text{mg}}{\text{mL}} \text{Co}^{2+}$, and diluted it by a factor of 10. We also noted that our EDTA solution contained 0.03066M EDTA dissolved in 3M NH_4OAc . We performed a practice titration first, using NH_4Cl to provide Cl^- ions and 10.00 mL of dilute cobalt standard to get

a feel for the average amount and specific colors of the titration (otherwise, these titrations were identical to the unknown ones). Next, we took our unknown cobalt solutions and used concentrated ammonia to neutralize the HCl in them (turning them from pink to reddish-brown), and 6M acetic acid to “un-neutralize” them back to a slightly-acidic pink. Next, we added 10.00 mL of EDTA standard (to excess), as well as 5 mL of 45% KSCN (our indicator) and 30 mL of acetone (which enhances the color of the indicator). Finally, we began the back-titration, adding dilute Co^{2+} standard until the solution very suddenly changed from vivid pink to an ashen blue. We recorded the amount of Co^{2+} standard used to neutralize, giving us enough information to find the excess quantity of EDTA, and thereby the amount of Co^{2+} unknown initially sequestered by EDTA.

3.3 Atomic Emission Spectroscopy of Cu^{2+} [3]

We began by acquiring our calibration standards of Cu^{2+} , containing 1.0, 2.0, 3.0, and 4.0 $\frac{\mu\text{g}}{\text{mL}}$ Cu^{2+} each in 0.2% HNO_3 . We also took 1 mL of each of our Cu^{2+} unknown solutions and diluted them by a factor of 100 (keeping in mind they had already been diluted one hundredfold at the end of week 1). We needed the concentrations of our samples to be between 1 and 5 $\frac{\mu\text{g}}{\text{mL}}$ Cu^{2+} for the AES to be accurate. With the help of lab staff, we aspirated a water blank, then the 1.0, 2.0, 3.0, and 4.0 $\frac{\mu\text{g}}{\text{mL}}$ standards for around 20 seconds each, as long as the AES took to calibrate them, taking down their intensities. Finally, we aspirated our three Cu^{2+} unknowns and noted down their intensities. We also noted that the AES was using a observing the spectra at a wavelength of 324.750 nm. With that, we had enough data to construct a calibration curve and find the concentration of our unknowns.

4 Results

4.1 Co^{2+} Concentration

Trial	Starting Volume (mL)	Ending Volume (mL)	Volume Change (mL)
Reference	15.7	27.1	11.4
1	27.1	40.7	13.6
2	13.6	27.4	13.8
3	27.4	41.8	14.4

Co^{2+} Standard Concentration: $9.26163 \frac{\text{mg}}{\text{mL}} \text{Co}^{2+}$

EDTA Standard Concentration: 0.03066M

4.1.1 Trial 1

$$\begin{aligned} & (0.03066 \frac{\text{mol}}{\text{L}} \text{Y} * \frac{1 \text{ L}}{1000 \text{ mL}} * 10.00 \text{ mL Y}) - ((40.7 \text{ mL} - 27.1 \text{ mL}) * 9.26163 \frac{\text{mg}}{\text{mL}} \text{Co}^{2+} * \frac{1 \text{ mL}}{10 \text{ mL}} * \frac{1 \text{ g}}{1000 \text{ mg}} * \\ & \frac{1 \text{ mol Co}^{2+}}{58.9332 \text{ g Co}^{2+}}) = 9.29 \times 10^{-5} \text{ mol Co}^{2+} \\ & \frac{9.29 \times 10^{-5} \text{ mol Co}^{2+}}{1 \text{ mL}} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{1000 \text{ mM}}{1 \text{ M}} = 92.9 \text{ mM} \end{aligned}$$

4.1.2 Trial 2

$$\begin{aligned} & (0.03066 \frac{\text{mol}}{\text{L}} \text{Y} * \frac{1 \text{ L}}{1000 \text{ mL}} * 10.00 \text{ mL Y}) - ((27.4 \text{ mL} - 13.6 \text{ mL}) * 9.26163 \frac{\text{mg}}{\text{mL}} \text{Co}^{2+} * \frac{1 \text{ mL}}{10 \text{ mL}} * \frac{1 \text{ g}}{1000 \text{ mg}} * \\ & \frac{1 \text{ mol Co}^{2+}}{58.9332 \text{ g Co}^{2+}}) = 8.97 \times 10^{-5} \text{ mol Co}^{2+} \\ & \frac{89.7 \times 10^{-5} \text{ mol Co}^{2+}}{1 \text{ mL}} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{1000 \text{ mM}}{1 \text{ M}} = 89.7 \text{ mM} \end{aligned}$$

4.1.3 Trial 3

$$\left(0.03066 \frac{\text{mol}}{\text{L}} \text{Y} * \frac{1 \text{ L}}{1000 \text{ mL}} * 10.00 \text{ mL Y} - ((41.8 \text{ mL} - 27.4 \text{ mL}) * 9.26163 \frac{\text{mg}}{\text{mL}} \text{Co}^{2+} * \frac{1 \text{ mL}}{10 \text{ mL}} * \frac{1 \text{ g}}{1000 \text{ mg}} * \frac{1 \text{ mol Co}^{2+}}{58.9332 \text{ g Co}^{2+}})\right) = 8.03 \times 10^{-5} \text{ mol Co}^{2+}$$

$$\frac{8.03 \times 10^{-5} \text{ mol Co}^{2+}}{1 \text{ mL}} * \frac{1000 \text{ mL}}{1 \text{ L}} * \frac{1000 \text{ mM}}{1 \text{ M}} = 80.3 \text{ mM}$$

4.1.4 Precision

$$\mu = \frac{x_1 + \dots + x_n}{n} = \frac{80.3 + 89.7 + 92.9}{3} \text{ mM} = 87.6 \text{ mM}$$

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} = \sqrt{\frac{1}{2} ((92.9 - 87.6)^2 + (89.7 - 87.6)^2 + (80.3 - 87.6)^2)} = 6.55 \text{ mM}$$

$$95\% \text{ conf. int.} = 87.6 \text{ mM} \pm (1.95996)(6.55 \text{ mM}) = [74.76, 100.44] \text{ mM} = 87.6 \text{ mM} \pm 14.7\%$$

*95% of a normal distribution is within 1.95996 standard deviations of the mean.

4.2 Cu²⁺ Concentration

4.2.1 Cu²⁺ Standard Intensities

Concentration (ppm)	Intensity (IU)
1	154675.35
2	309714.70
3	471167.16
4	624953.22

4.2.2 Cu²⁺ Unknown Intensities

Sample	Intensity (IU)
1	189462.37
2	186707.78
3	191474.78

$$\lambda = 324.750 \text{ nm}$$

4.2.3 Least-Squares Determination of Calibration Curve

$$\text{Slope: } m = \frac{\left| \begin{array}{cc} \Sigma(x_i y_i) & \Sigma x_i \\ \Sigma y_i & n \end{array} \right|}{\left| \begin{array}{cc} \Sigma(x_i^2) & \Sigma x_i \\ \Sigma x_i & n \end{array} \right|} = 157228.61$$

$$\text{Intercept: } b = \frac{\left| \begin{array}{cc} \Sigma(x_i^2) & \Sigma x_i y_i \\ \Sigma x_i & n \end{array} \right|}{\left| \begin{array}{cc} \Sigma(x_i^2) & \Sigma x_i \\ \Sigma x_i & n \end{array} \right|} = -2943.91$$

$$r^2 = 0.999916$$

$$\text{For Intensity } I \text{ (IU) and Concentration } C \text{ (ppm)} \quad I = 157228.61C - 2943.91C = \frac{(I+2943.91)}{157228.61}$$

Uncertainty of the Least-Squares Method Because the correlation coefficient for this regression is so high (0.999916), I have elected to dismiss any uncertainty inherent in the regression process as minimal. This is definitely because these numbers are beyond the scale of uncertainty, and not because I don't want to typeset even more equations.

MP-AES Cu(II) Calibration Curve

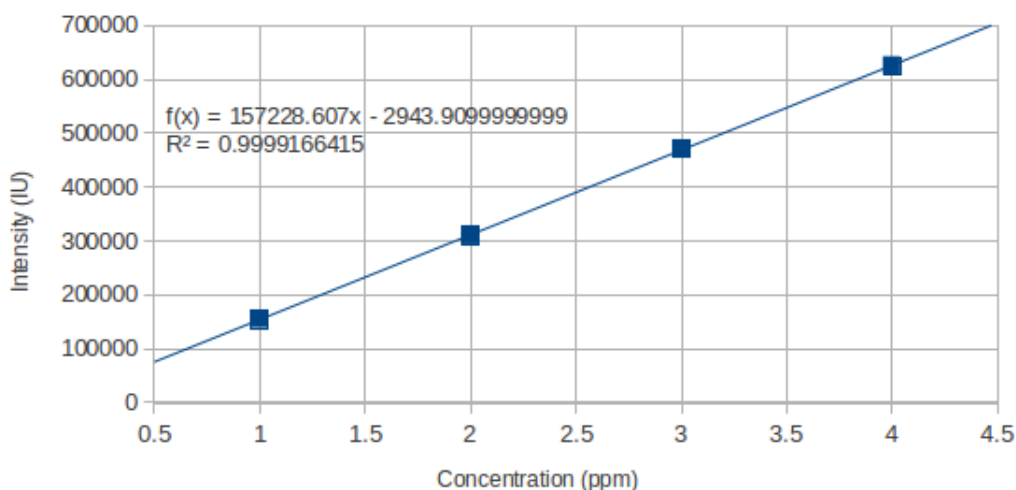


Figure 4: AES Calibration Curve and Least-Squares Trendline

4.2.4 Calculating Unknown Concentrations

$$\mu = \frac{x_1 + \dots + x_n}{n} = \frac{189462.37 + 186707.78 + 191474.78}{3} \text{mM} = 189214.98 \text{ IU}$$

$$\sigma = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} =$$

$$\sqrt{\frac{1}{2}((189462.37 - 189214.98)^2 + (186707.78 - 189214.98)^2 + (191474.78 - 189214.98)^2)} = 2393.1099 \text{ IU}$$

$$95\% \text{ conf. int.} =$$

$$189214.98 \text{ IU} \pm (1.95996)(2393.1099 \text{ IU}) = [184524.58, 193905.38] \text{ IU} = 189214.98 \text{ IU} \pm 2.47887\%$$

*95% of a normal distribution is within 1.95996 standard deviations of the mean.

$$C = \frac{(I + 2943.91)}{157228.61}$$

$$C = \frac{([184524.58, 193905.38] + 2943.91)}{157228.61}$$

$$C = [1.19233, 1.25199] \text{ ppm} = 1.22216 \pm .02983 \text{ ppm} (\pm 2.47887\%)$$

$$[1.19233, 1.25199] \text{ ppm} = [1.19233, 1.25199] \frac{\text{mg}}{\text{kg}} * \frac{1 \text{ kg}}{1 \text{ L}} * \frac{1 \text{ g}}{1000 \text{ mg}} * \frac{1 \text{ mol}}{63.546 \text{ g}} * \frac{1000 \text{ mmol}}{1 \text{ mol}} * \frac{10,000 \text{ mL dilute}}{1 \text{ mL concentrated}} = [187.633, 197.021] \text{ mM Cu}^{2+} = 192.3272 \text{ mM} \pm 2.47887\%$$

5 Conclusions

In this lab, we toyed with various methods of Quantitative Analysis, which gave us a perspective on some possible methods of approaching quantitative analysis, and their relative precisions. We hypothesized that Atomic Emission Spectroscopy would produce a smaller error than Complexometric Titration, due to its far more objective measurements and the fact that human error was practically nonexistent. While the Complexometric Back-titration retained a percent error of around 14, the AES produced a fit so high that it was effectively discarded, and all error in the final measurement came from variation in the amounts of copper analyzed—human error, inherent in the ion-exchange chromatography portion of the lab (and not the AES analysis). Both of our results are near the same order of magnitude, one that is neither ridiculously high nor impossibly low.

This is not to say that there were not several errors that tainted our otherwise pure results. Our third attempt at complexometric titration was plagued by a myriad of problems that left it lying quite off from the other two, rather consistent titrations. Due to what appeared to be a mixing of the reagents in the wrong order, the sample turned various colors before developing an oily film and separating into layers, though somehow the addition of KSCN indicator solved all these problems and allowed the titration to proceed relatively normally. However, this data point classifies as an outlier, its value being several standard deviations above the average of the other two data points. Another possible source of error involves the separation of copper and cobalt through the anion-exchange chromatography; because the column was not long enough to allow for significant separation, the two bands arrived relatively close to each other, meaning that a certain amount of overlap would be inevitable. While cobalt in the copper solution would not emit at the same wavelengths and hence would not be detected by the AES, copper in the cobalt solution would be sequestered by EDTA along with the cobalt, leading to a false increase in the reported concentration of cobalt. In conclusion, this lab was a great exercise in the variety of tools, options, and instruments available to an analytical chemist in finding the contents and concentrations of an unknown solution. I would greatly enjoy a similar lab in which more freedom of choice was given to the analytical methods to be used to isolate and quantify the unknown compounds.

References

- [1] UC Berkeley bSpace: *Quantitative Analysis of a Solution Containing Cobalt and Copper (Part 1)*. <https://bspace.berkeley.edu/access/content/group/8fc376df-c082-4a38-a00d-f84a8a6d8945/Lab%20Manual/Exp1%20Cu%2CCo%20separation%20Sp13.pdf> (Accessed February 15, 2012)
- [2] UC Berkeley bSpace: *Quantitative Analysis of a Solution Containing Cobalt and Copper (Part 2)*. <https://bspace.berkeley.edu/access/content/group/8fc376df-c082-4a38-a00d-f84a8a6d8945/Lab%20Manual/Exp2%20Cu%2CCo%20EDTA%20titration%20Sp13.pdf> (Accessed February 15, 2012)
- [3] UC Berkeley bSpace: *Quantitative Analysis of a Solution Containing Cobalt and Copper (Part 3)*. <https://bspace.berkeley.edu/access/content/group/8fc376df-c082-4a38-a00d-f84a8a6d8945/Lab%20Manual/Exp3%20CuCo%20MP-AES%20Sp13.pdf> (Accessed February 15, 2012)
- [4] Ion-Exchange Chromatography image: http://chemwiki.ucdavis.edu/api/deki/files/6992/ion_exch.jpg (edited by author) (Accessed February 15, 2013)
- [5] EDTA image: <http://upload.wikimedia.org/wikipedia/commons/0/09/Metal-EDTA.svg>, <http://upload.wikimedia.org/wikipedia/commons/3/3c/EDTA.svg> (merged and edited by author) (Accessed February 15, 2013)
- [6] Atomic Emission Spectroscopy image: <http://kinardf.people.cofc.edu/Applets/AtomicSpectroscopyAnimation.gif>